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(21) International Application Number: PCT/US91/08818 (22) International Filing Date: 3 December 1991 (03.12.91) (30) Priority data: 623,013 6 December 1990 (06.12.90) US (71) Applicant: THE WESTERN COMPANY OF NORTH AMERICA [US/US]; 515 Post Oak Blvd., Suite 1200, Houston, TX 77027 (US). (72) Inventors: SATYANARAYANA GUPTA, D., V. ; 11 Swallow Trail Court, The Woodlands, TX 77381 (US). COONEY, Aiden ; 12000 Sawmill Rd. #2814, The Woodlands, TX 77380 (US).		(74) Agents: BIELINSKI, Peter, A.; The Western Company of North America, 515 Post Oak Blvd., Suite 1200, Houston, TX 77027 (US) et al. (81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), HU, IT (European patent), LU (European patent), MC (European patent), NL (European patent), NO, RO, SE (European patent), SU*. Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: ENCAPSULATIONS FOR TREATING SUBTERRANIAN FORMATIONS AND METHODS FOR THE USE THEREOF (57) Abstract Encapsulations comprised of a breaker enclosed within a membrane are utilized to break fluids used to fracture subterranean formations. The membrane of the encapsulation is permeable to at least one fluid in the subterranean formation or injected with the breaker such that the breaker diffuses through the membrane into the fracturing fluid. Thus, controlled amounts of breaker are released into the fracturing fluid.		

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Encapsulations for Treating Subterranean
Formations and Methods for the Use Thereof

Technical Field

The invention relates to methods for treating
5 subterranean formations. Specifically, the
invention is directed to a composition used to
fracture subterranean formations and methods for
the use thereof. Further, the invention is
directed to methods of fracturing a subterranean
10 formation utilizing a fracturing composition which
includes an encapsulated breaker.

Background Art

It is a common practice to treat subterranean
formations to increase the gross permeability or
15 conductivity of such formations by procedures
which are identified generally as fracturing
processes. For example, it is a conventional
practice to hydraulically fracture a well in order
to produce one or more cracks or "fractures" in
20 the surrounding formation by mechanical breakdown
of the formation. Fracturing may be carried out
in wells which are completed in subterranean
formations for virtually any purpose. The usual
candidates for fracturing, or other stimulation
25 procedures, are production wells completed in oil
and/or gas containing formations. However,
injection wells used in secondary or tertiary
recovery operations, for example, for the
injection of water or gas, may also be fractured
30 in order to facilitate the injection of fluids
into such subterranean formations.

Hydraulic fracturing is accomplished by
injecting a hydraulic fracturing fluid into the

well and imposing sufficient pressure on the fracturing fluid to cause the formation to break down with the attendant production of one or more fractures. The fracture or fractures may be
5 horizontal or vertical, with the latter usually predominating, and with the tendency toward vertical fracture orientation increasing with the depth of the formation being fractured. Usually a gel, an emulsion or a foam, having a proppant
10 such as sand or other particulate material suspended therein is introduced into the fracture. The proppant is deposited in the fracture and functions to hold the fracture open after the pressure is released and the fracturing fluid is
15 withdrawn back into the well. The fracturing fluid has a sufficiently high viscosity to penetrate into the formation to realize fracturing and to retain the proppant in suspension or at least to reduce the tendency of the proppant to
20 settle out of the fracturing fluid. Generally, a gelation agent and/or an emulsifier is used to gel or emulsify the fracturing fluid to provide the high viscosity needed to realize the maximum benefits from the fracturing process.

25 After the high viscosity fracturing fluid has been pumped into the formation and the fracturing of the formation has been obtained, it is desirable to remove the fluid from the formation to allow hydrocarbon production through the new
30 fractures. Generally, the removal of the highly viscous fracturing fluid is realized by "breaking" the gel or emulsion or, in other words, by converting the fracturing fluid into a low viscosity fluid. Breaking the gelled or
35 emulsified fracturing fluid has commonly been

obtained by adding a "breaker," that is, a viscosity-reducing agent, to the subterranean formation at the desired time. However, this technique can be unreliable and sometimes results in incomplete breaking of the fluid and/or premature breaking of the fluid before the fracturing process is complete. Premature breaking can decrease the number of fractures obtained and thus, the amount of hydrocarbon recovery. Further, it is known in the art that most fracturing fluids will break if given enough time at sufficient temperature and pressure. However, it is, of course, most desirable to return the well back to production as quickly as possible.

It has been suggested that fracturing fluid is concentrated 5-7 times due to fluid loss during pumping and fracture closure. G.S. Penny, "An Evaluation of the Effects of Environmental Conditions in Fracturing Fluids Upon the Long term Conductivity of Proppants," SPE 16900, Presented at 62nd Annual Technological Conference of SPE, Dallas, Texas, September 27-30, 1987. Further, others have emphasized the effects of filter cake upon conductivity. M.A. Parker and B.W. McDaniel, "fracturing Treatment Designs Improved by Conductivity Measurements Under Incite to Conditions," SPE 16901, Presented at 62nd Annual Technological Conference of SPE, Dallas, Texas, September 27-30, 1987; B.W. McDaniel and M.A. Parker, "Accurate Design and Fracturing Treatment Refines Conductivity Measurement at Reservoir Conditions," SPE 17541, Presented at SPE Rocky Mountain Regional Meeting, Casper, Wyoming, May 11-13, 1984. An unencapsulated breaker dissolves

in the fluid and is lost along with the fluid during fluid loss. The dissolved breaker does not concentrate along with the filter cake concentration of the polymer and thus does not effectively break the filter cake. Therefore, permanent damage to the formation occurs.

There have been several proposed methods for the breaking of fracturing fluids which were aimed at eliminating the above problems. For example, U.S. Patent No. 4,202,795 discloses a method to release a chemical into an aqueous fluid by combining the chemical with a solid hydratable gelling agent and a breaker for the gel formed by the gelling agent when hydrated. The mixture is formed into prills or pellets, preferably having a size and range of from about 20 to about 40 mesh. (U.S. Sieve Series) From combining the pellets with an aqueous fluid into which the chemical is to be released, the gelling agent in the pellets hydrates and forms a protective gel around each of the pellets which prevents the release of the chemical into the aqueous fluid for the time period required for the protective gel to be broken by the gel breaker in the pellets. Once the gel breaker has broken the protective gel, the chemical in the pellets is released into the aqueous fluid. The time required for the protective gel to be broken is varied by varying the quantities of hydratable gelling agent and the gel breaker utilized in the pellets and by using different gelling agents and gel breakers. A large amount of hydratable gelling agent is required and the amount of hydratable gelling agent must be monitored closely.

U.S. Patent No. 4,506,734 also provides a

method for reducing the viscosity and the resulting residue of an aqueous or oil based fluid introduced into a subterranean formation by introducing a viscosity-reducing chemical contained within hollow or porous, crushable and fragile beads along with a fluid, such as a hydraulic fracturing fluid, under pressure into the subterranean formation. When the fracturing fluid passes or leaks off into the formation or the fluid is removed by back flowing, any resulting fractures in the subterranean formation close and crush the beads. The crushing of the beads then releases the viscosity-reducing chemical into the fluid. This process is dependent upon the pressure of the formation to obtain release of the breaker and is thus, subject to varying results dependent upon the formation and its closure rate.

U.S. Patent No. 4,741,401 discloses a method for breaking a fracturing fluid comprised of injecting into the subterranean formation a capsule comprising an enclosure member containing the breaker. The enclosure member is sufficiently permeable to at least one fluid existing in the subterranean environment or injected with the capsule such that the enclosure member is capable of rupturing upon sufficient exposure to the fluid, thereby releasing the breaker. The patent teaches that the breaker is released from the capsule by pressure generated within the enclosure member due solely to the fluid penetrating into the capsule whereby the increased pressure causes the capsule to rupture, i.e., destroys the integrity of the enclosure member, thus releasing the breaker. This method for release of the

breaker would result in the release of the total amount of breaker contained in the capsule at one particular point in time. The patent examples disclose the use of the encapsulated breaker at
5 temperatures ranging from room temperature, 65°C to 85°C.

In another method to release a breaker, U.S. Patent No. 4,770,796 teaches or suggests an acid fracturing fluid composition comprising a polymer,
10 a crosslinking agent for said polymer, an aqueous acid and a breaker compound capable of coordinating with titanium or zirconium crosslinking agent. The breaker compound is encapsulated in a composition comprising a
15 cellulosic material and a fatty acid and optionally a wax.

Further, U.S. Patent No. 4,919,209 discloses a proposed method for breaking a fluid. Specifically, the patent discloses a method for
20 breaking a gelled oil fracturing fluid for treating a subterranean formation which comprises injecting into the formation a breaker capsule comprising an enclosure member enveloping a breaker. The enclosure member is sufficiently
25 permeable to at least one fluid existing in the formation or in the gelled oil fracturing fluid injected with the breaker capsule, such that the enclosure member is capable of dissolving or eroding off upon sufficient exposure to the fluid,
30 thereby releasing the breaker. Thus, disclosing a method for the total release of the complete amount of breaker contained within the capsule at one particular time and the enclosure member does not stay intact, it dissolves or erodes.

35 There remains a need for a method for the

controlled breaking of fracturing fluids which is more economical and provides not only controlled release of the breaker, reduces damage to the formation and facilitates well clean-up.

5 Disclosure of Invention

 The invention relates to a method for treating a subterranean formation. specifically, the invention is directed to a method of fracturing a subterranean formation utilizing an aqueous-based fracturing fluid and controllably
10 breaking said fluid with an encapsulated breaker. The present invention is also directed to a composition for fracturing a subterranean formation which includes the utilization of an
15 encapsulated breaker. The present invention is further directed to an encapsulated breaker for controllably breaking aqueous-based fracturing fluids.

 The encapsulated breaker of the invention is
20 comprised of a breaker enclosed within an inert membrane which is permeable to at least one fluid in the subterranean formation or to a carrier fluid injected with the encapsulated breaker such that upon sufficient contact with one of the
25 fluids, the breaker is controllably released over time by diffusion through the membrane into the fracturing fluid. The membrane stays intact throughout the period of the release of the breaker, thus providing controlled release.

30 Using the method of the present invention there is provided a means of slowly releasing amounts of breaker over time instead of a single release of the total amount of breaker from all capsules at a given time. Further, utilizing the

method of the present invention provides an encapsulation membrane made of a single component which obtains the above results without the need for additional components which can increase the cost of the fracturing process. The present invention also provides an encapsulated breaker which is capable of functioning in an aqueous-based fluid at high temperatures, from about 80°F to about 350°F, without premature release of the breaker into the fracturing fluid. Further, the present invention provides increased well clean-up due to the fact that the encapsulation membrane stays intact, i.e., it does not degrade, dissolve, erode or rupture, thus maintaining the integrity of the membrane. The encapsulated breaker of the present invention provides these benefits due to the fact that the breaker is dissolved inside the capsule by permeating fluid and subsequently diffuses in a controlled manner through the membrane into the formation being treated with the fracturing fluid. In addition, the encapsulation which has partially released the enclosed breaker becomes entrapped within the filter cake formed by the gelled/emulsified fracturing fluid upon water leak-off into the formation. Even after load water recovery, the capsule continues to release the breaker which breaks the gel/emulsion residue and hence results in decreased formation damage.

Best Mode for Carrying Out the Invention

The method of the present invention is directed to the fracturing of subterranean formations with aqueous-based fracturing fluids which are known in the art. For example, the method of the present invention is directed to

fracturing subterranean formations using aqueous-based fracturing fluids containing polymers such as guar, hydroxy alkyl guar, carboxy alkyl hydroxy guar, cellulose, hydroxy alkyl cellulose, carboxy alkyl hydroxy alkyl cellulose, xanthan and the like. The present invention is also directed to fracturing fluids which are crosslinked. For example, fracturing fluids which are crosslinked with known crosslinkers like borate, titanate, and zirconate. Specifically, the method of the present invention is directed to injecting a subterranean formation with a fracturing fluid as disclosed above, fracturing the formation, and controllably breaking the fracturing fluid by utilizing the encapsulated breaker of the invention.

Generally, the encapsulated breaker of the present invention can be added to any fracturing fluid generally known in the art. In the practice of the present invention, the encapsulated breaker can be injected with the fracturing fluid. Further, the encapsulated breaker of the present invention can be added to a carrier fluid and then injected into the subterranean formation subsequent to, simultaneous with, or prior to the injection of the fracturing fluid. Encapsulated breakers are often added with the fracturing fluid. The various fluids used to fracture formations and their compositions are well known in the art and essentially contain a carrier fluid, usually an aqueous liquid, and a viscosifying polymer. Fracturing fluids usually also contain one or more of the following: surfactants, salts, anti-foaming agents, and polymer thickeners.

The encapsulated breaker of the present invention is made utilizing known microencapsulation techniques. For example, the encapsulated breaker of the present invention can be made utilizing a fluidized bed process known as the Wurster process. See U.S. Patent Nos. 3,237,596 and 3,382,093. Further, the encapsulated breaker of the present invention can be made by interfacial polymerization. See U.S. Patent No. 3,577,515. The interfacial polymerization may involve reaction between two reactants to create a polymeric membrane or may involve crosslinking a linear polymer deposited around the breaker with known crosslinkers to effectively control the diffusion mechanism. Further, the crosslinked densities of the membrane can be varied.

The procedure for preparing the capsules of the present invention by interfacial polymerization or crosslinking is as follows: In a 1 liter beaker agitated with a turbine type stirrer, either an oil soluble monomer like sebacoyl chloride or an ethylene copolymer like Microtek Polymer CRP-1000 (Microtek Laboratories, Dayton, Ohio) is dissolved in an organic solvent, for example, toluene. Heat is used, if necessary, for faster dissolution. A non-solvent type of oil, such as vegetable oil, is added and partially cooled to create an emulsion. The breaker is added and cooling is continued. In the case of ethylene copolymer with the breaker potassium persulfate, the copolymer coats the persulfate particles as a complete and uniform coating. The other reactant such as hexamethylene diamine (for interfacial polymerization process) or a

crosslinking agent (for interfacial crosslinking process) such as Microtek CRX-1000 (Microtek Laboratories, Dayton, Ohio) is added and stirred until complete polymerization and/or cure is
5 obtained. After filtering, the capsules are washed with a quick-drying solvent, like toluene or isopropanol, to remove the oil. Upon drying, dry flowable microcapsules are obtained.

The membrane of the encapsulated breaker of
10 the present invention can be made out of any polymer which will not react with the enclosed breaker, i.e., inert to the enclosed breaker or is not degradable by the enclosed breaker but is permeable to at least one fluid in the
15 subterranean formation whether it be a component of the fracturing fluid, a fluid native to the formation, or a carrier fluid injected with the encapsulated breaker. The carrier fluid can be a brine solution, a brine solution containing a
20 dissolved or hydrated natural polymer of the like. Further, the membrane of the encapsulated breaker of the present invention must not react with, i.e., is inert to the fracturing fluid and any fluids in the subterranean formation such that the
25 membrane does not degrade, dissolve and is not destroyed.

In the practice of the present invention, polyamides, crosslinked ethylene copolymers and cellulosic materials are preferred materials which
30 can be used as membranes to encapsulate the breaker. Of the polyamides, preferably nylon is utilized. The nylon useful in the practice of the present invention includes nylon 6, 9, 12, 66 and mixtures thereof. As for cellulosic materials
35 which can be used in the practice of this

invention, preferably ethylcellulose and methylcellulose are utilized. Most preferably, ethylcellulose is used.

5 In the practice of the present invention, any known breaker can be used which does not react with and/or degrade the encapsulating membrane. Alkali and alkaline earth persulfates, percarbonates or perchlorates may be used as
10 breakers. Preferred breakers include alkali and alkaline earth metal persulfates. Further, ammonium persulfate may also be utilized. Most preferably, potassium persulfate is used in the practice of the present invention. In terms of the total weight percent of each capsule,
15 generally from about 20% to about 90% of the total weight is actual breaker. In the practice of the present invention, depending upon the temperature of the formation and the desired time of breaking, the fracturing composition of the present
20 invention can contain a breaker in an amount from about 0.1 pounds per thousand gallons of total volume of fracturing fluid to about 50 pounds per thousand gallons of total fracturing fluids. Further, under certain conditions breakers in
25 amounts over 50 pounds per thousand gallons of total fracturing fluid may be used.

As stated, the encapsulated breakers are made by known encapsulation techniques such as a fluidized bed process and/or interfacial
30 polymerization. Generally, the encapsulated breaker is made having a membrane of a certain thickness and permeability to obtain the desired controlled release of the breaker for the particular fracturing process. The amount of
35 breaker contained within, i.e., enclosed within

the membrane can vary depending upon the desired release. Thus, the size of the encapsulated breaker varies depending upon the desired amount of breaker to be released and the desired rate at which the breaker is to be released. For example, the thicker the membrane, the longer it takes for the permeation of fluid through the membrane into the capsule and thus, dissolution of the breaker, and diffusion of the breaker through the membrane wall thus, contacting the breaker with the fracturing fluid. In the practice of the present invention, depending upon the desired release time, a membrane thickness from about 5 to about 25 microns has been found to be useful.

Further, the larger the diameter of the encapsulated breaker, that is, the greater amount of breaker enclosed, assuming the thickness of the membrane stays the same, the greater the surface area, thus increasing the surface area for permeation and diffusion, thereby increasing the rate of contacting the breaker with the fracturing fluid. The release of the breaker will not only depend upon the type of membrane and its thickness but also upon the type of fracturing fluid, the fluids present in the formation and the temperature of the formation. The size or diameter of the encapsulated breaker can vary from about 50 μm to about 420 μm . Generally, the size or diameter of the encapsulated breaker should be close to or smaller than the size of the proppant utilized, i.e., the carrying capacity of the fluid, the viscosity, is set up to transport particles, including proppant and breaker, of a certain diameter and size. If the encapsulated breaker is smaller than the proppant, then the

breaker can be trapped within the filter cake and/or proppant pack for continued release thus reducing formation damage. For example, with 20 to 40 mesh proppant, an encapsulated breaker of 140-840 microns would be useful in the present invention.

In the present invention, the breaker encapsulated within the membrane is released from within the membrane by diffusion. Fluid moves from outside the membrane into the membrane dissolving the breaker. The breaker is then slowly released back through the membrane by diffusion. The breaker is released due to the fact that the breaker solution concentration within the capsule, i.e., within the membrane, slowly becomes greater than the breaker solution concentration outside the capsule, i.e., outside the membrane, and osmotic pressure transfers the breaker through the encapsulation membrane, thus contacting the breaker with the fracturing fluid and subsequently breaking the fluid.

EXAMPLES

The encapsulated breakers of the present invention were made using the interfacial polymerization process having a nylon coating as previously described herein. The encapsulated breaker varied in size, weight percentage of breaker, form, and percentage active breaker contained therein as set forth in Table 1. These encapsulations contained potassium persulfate breaker and the encapsulation membrane was prepared with varying crosslinked densities. The release percentage at 190°F was determined by the following method: (1) placing 170 ml of distilled water in each of four 250 ml glass containers

labeled 1-4; sealing the containers with lids and placing the containers in a constant temperature ethylene glycol bath; the temperature was constant at 190°F with the glycol level being maintained at the same level of the fluid in the containers; (2) one gram of encapsulated breaker was weighed out to the nearest 0.1 mg using weighing paper; the encapsulated breaker was transferred to a piece of silk screen and carefully tied with fine wire to form a bag; the bag was weighted to the nearest 0.1 mg to obtain the initial bag weight; four bags were prepared in the above manner and labeled 1-4; (3) after the temperature of the bath was equilibrated at 190°F for at least 15 minutes, the bags were placed into each of the corresponding labeled containers and the lids were replaced; (4) in 1 1/2 hours, the bag labeled number 1 was removed using forceps and replacing the lid on the container; the bag was rinsed under running distilled water for about 20 seconds; the bag was then placed in a 100°C oven for 1 1/2 hours; the bag was then weighed immediately upon removal from the oven and the final bag weight was recorded; (5) step number 4 was repeated for each bag at interval times of 1, 2 and 4 hours; immediately after the four hours, the four containers were removed from the bath and allowed to cool to room temperature; these containers were then set aside for conductivity measurements. The percentage release of breaker at 190°F was determined as follows: (1) % capsule weight loss = (initial bag weight - final bag weight) X (times) 100% divided by the weight of the encapsulated breaker sample; (2) % core loss = % capsule weight loss at time t X (times) 100% divided by the percentage of

capsule weight loss at 4 hours.

The percentage released for each batch at 2, 4 and 6 hours was determined by using the following method: The percent of persulfate released was calculated by dividing the conductivity of the fluid at time t times 100%, divided by the conductivity of the fluid at four hours. The conductivity meter was thoroughly washed with distilled water. The conductivity of each of the labeled containers was measured after cool down to room temperature from 190°F. Starting with the container labeled number 1 (1/2 hour) and progressing to the container labeled number 4 (4 hours). The contents of each container was weighed to determine any significant loss of water.

Table 1 illustrates the controlled release of the breaker in the practice of the present invention:

TABLE 1

Batch No.	Crosslink Density***	Initial Particle Size Microns	Wt % Core	Form	% Active	% Released Hrs.*			190°F Release***	
						2	4	6		
5	1	M	50-450	80.8	Powder	80.8	50.9	61.3	67.8	69.9
	2	M	50-450	80.8	Powder	80.8	16.7	27.8	42.2	80.8
	3	L	100-420	80.8	Powder	80.8	31.5	44.9	50.2	70.0
	4	L	100-420	80.8	Powder	80.8	19.2	28.1	34.2	60.3
10	5	H	100-420	78.0	Powder	78.0	9.3	14.7	18.4	29.3
	6	M	100-420	80.8	Powder	80.8	43.5	54.8	57.9	37.2
	7	M	100-420	74.0	Powder	74.0	11.3	18.8	22.9	15.5
	8	H	150-420	78.0	Powder	78.0	12.3	19.1	21.9	19.0
	9	M	100-420	70.0	Powder	70.0	(No measurement)			16.1

* Fifty degrees centigrade - conductivity method.

15 ** Determined by amount of crosslinker added and by observation, low = L, medium = (M), high = (H).

*** Determined by measuring weight loss in water (1 gram in 170 ml) at 190°F in 1/4 hour.

A series of rheology and proppant transport evaluations were conducted to evaluate the encapsulated breaker of the present invention. Two samples were tested. Sample 1 consisted of
5 encapsulated potassium persulfate enclosed within a membrane of crosslinked polyethylene. The sample had a membrane thickness from about 80 μm to about 20 μm . The size distribution of the encapsulation was from about 20 to about 200 mesh
10 (U.S. Series). The active breaker within the encapsulation was between 75% to about 85%. Sample 2 consisted of potassium persulfate encapsulated within a membrane of ethylcellulose. The membrane had a thickness from about 8 μm to
15 about 20 μm . The encapsulation ranged in size from about 20 to about 200 mesh (U.S. Series). The percentage of active breaker contained was between 75% and 85%. The tests were run with 35 pounds Guar and Borate crosslinked fluid at pH of
20 10 after shear history simulation in field mixing equipment. This fluid, in absence of breaker, showed no proppant settling.

A Guar gel was hydrated in a 1,000 gallon tank and sent to a blender where the proppant was
25 added. The slurry was pumped through an intensifier, then through a static mixer where a crosslinker, borate, was added. The fluid was directed through 3,000 feet of 1 inch coil tubing through a choke at a splitter table where the
30 slurry was split and routed in two directions. Most of the fluid was directed to a fluid separator, about 5 gallons per minute was directed to the formation shear and heat-up simulator. The fluid routed to the formation shear simulator was
35 heated to a test temperature and sheared at 40 to

50/seconds for 30 minutes. After being so conditioned, measurements were conducted with a pipe rheometer, flowmeter, densiometer, and a 20 foot slot rheometer.

5 The mixing equipment consisted of fracturing tanks, a blending unit, an intensifier, and a heated coiled tubing unit. The mixing tank was a 750 gallon round tank in which the base gel was mixed by circulating with a centrifugal pump
10 running between the blender and the fluid tank. During the mixing procedure, the base polymer, Guar, was slurried in isopropanol at a concentration of 4 pounds per gallon. The slurry was then added to the fluid while circulating
15 through the blender and the round tank. During the mixing procedure, 2% potassium chloride was added to the water while circulating as well as biocide. The polymer was then added in the form of alcohol slurry to water and the fluid was
20 circulated until the desired viscosity was reached. The fluid pH and the viscosity were measured and recorded.

 During the run the base polymer was charged into the section manifold of the intensifier pump
25 at 125 psi. A dual piston Jaeco pump was used to pump the crosslinker, 16% sodium hydroxide, on the high pressure side of the intensifier pump. The flow rate was monitored at the high pressure side so that adjustment of the crosslinker rate could
30 be made.

 Tubing shear was simulated by pumping through 3,000 feet of 1 inch coiled tubing. Internal diameter of the tubing was .89 inches. The rate of 25 gallons per minute or 0.6 bbl per minute
35 corresponds to a velocity of 13 feet per second

and a Reynolds number of 89,500 for water and 5,008 for gel. A Reynolds number of 5,000 is on the upper end of the transition zone when going to full turbulence and 10,000 would be fully developed.

In the reported evaluations the 35 pound Guar plus Borate plus 2 ppg encapsulated breaker was first run with a small amount of marker proppant (black 20/40 mesh sand). In this manner, rheology with essentially no proppant was measured as well as single grain settling velocities. If the marker proppant run was successful, a run was conducted with 2 ppg 20/40 sand. Settling velocities were measured at the end of the high shear period before heat up (blue tank) and after flowing through the slot at temperature.

The results are summarized in Table 2. The settling data after shear history and heat up are set forth in Table 2. With no breaker there is no settling in any point in the system. With 2 ppg of Sample 1 there is no observed settling after the Tubing simulator indicating no premature breaker release with marker proppant and 2 ppg sand. After heat up, a settling rate of .21 inches/minute was observed at the end of the slot with marker proppant; the settling rate doubled with 2 ppg sand to .42 inches/minute. Sample 2 had higher settling rates; marker proppant settled at .7 inches/minute at the end of the slot and 2 ppg 20/40 sand settled at 1.68 inch/minute or 4 times the rate of Sample 1.

While transporting 2 ppg sand through the slot, the transport was affected at 150°F by 2 ppg breaker. This was true for both samples 1 and 2. A dynamic settling velocity was on the average of

1.5 inch/minute for Sample 1 and 3 inch/minute for Sample 2. The estimated dynamic stability of the gels at 150°F was 45 minutes with Sample 1 and 30 minutes and Sample 2.

5 Samples taken before heat up (blue tank) were placed in an oven at 150°F to observe settling. Over the course of 2 hours no settling was observed for Sample 1 and only a minor amount of settling was seen in Sample 2. Broken fluid
10 developing around each capsule was observable. Between 8 and 12 hours both samples were completely broken.

TABLE 2

15 35ppt Guar + 1.2ppt Borate
 pH to 10 With NaOH
 Indicated Breaker at 2ppt
 Temperature 150°F

	Sample 1	Sample 2	Standard	40ppt Base Gel
	Settling Rate	Settling Rate	Settling Rate	Settling Rate
	<u>in/min</u>	<u>in/min</u>	<u>in/min</u>	<u>in/min</u>
	Marker Proppant			
25	After Tubing (100°F)	n/o	n/o	9.8
	End of Slot (150°F)	0.21	0.7	n/o
	2ppg 20/40 Sand			
	After Tubing (100°F)	n/o	0.014	n/o
	End of Slot	0.42	1.68	n/o
30	Dynamic Settling note at 50/sec	1.5	3	n/o

n/o = none observed in first 5 minutes

35 Table 3 illustrates the mechanism by which breaker is released from the encapsulation of the present invention. One gram of breaker of each Sample 1 and Sample 2 was added to 170 ml of distilled water and placed in a 190°F water bath.

Observations were made under a light microscope (Carl Zeiss #475003-9903) at 0.5, 1.5, 2.5, 3.5, 4 and 6 hours.

TABLE 3

Time	Observation	
	Sample 1	Sample 2
0.5 hr.	No rupturing.	No rupturing.
1.5 hr.	No rupturing. Capsules clumped together. Remain spherical.	No rupturing. Capsules clumped together. Remain spherical.
2.5 hr.	No rupturing. Slight deflated balloon appearance.	Deflated balloon appearance. No rupturing.
3.5 hr.	No rupturing. Capsules remaining intact. Slight deflated balloon appearance.	Deflated balloon appearance. No rupturing.
4.0 hr.	Capsules slightly deflated. No rupturing.	Large extent of deflation. No rupturing.
6.0 hr.	No rupturing. Capsules still spherical in appearance.	Majority of capsules greatly deflated in appearance. No rupturing.

Table 4 illustrates that the encapsulated breaker of the present invention reduces filter cake residue. The following core testing was performed. Berea sand core samples of approximately 50 millidarcies were dried in a convection oven at 160°F. The core samples were evacuated and pressure saturated with 2% potassium chloride brine. The cores were stored under the brine prior to testing. The samples were loaded in hydrostatic core holders at approximately 1200 psig net overburden pressure at 160°F. Potassium

chloride brine was flushed through the cores in forward and reverse flow directions at 300 psig back pressure. Forty ppt hydroxypropyl guar gelled in potassium chloride brine was flowed over (for approximately 35 pore volumes) through core in forward direction to build filter cake. Differential pressure was monitored at constant flow rate. This was performed on samples at the following encapsulated breaker loadings:

- 10 a) control sample - no breaker
- b) 2 ppt gallons
- c) 5 ppt gallons
- d) 10 ppt gallons
- e) 20 ppt gallons.

15 The samples were allowed to set at temperature (160°F) for two hours after a peak differential pressure of approximately 800-1000 psig. Afterwards, 2% potassium chloride brine was flushed through the sample in the forward direction at constant flow rate for 53 to 76 pore volumes, while the differential pressure was monitored. The core was allowed to set overnight at 160°F at minimal flow rate so as to not dehydrate the filter cake. Two percent potassium chloride brine was flushed through the sample in the forward direction at constant flow rate for less than 5 pore volumes, while the differential pressure was monitored. Finally, 2% potassium chloride brine was flushed through the sample in the reverse direction at constant flow rate while the differential pressure was monitored. The results were shown in Table 4, which shows the normalized differential pressure as a function of pore volume of flow. The normalized differential pressure is obtained by dividing the differential

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pressure by the peak differential pressure. In the case of the control test (with no breaker present), the pressure builds due to the build-up of the filter cake which is not broken on flushing; and even after approximately 250 pore volumes of flow, the pressure differential is still approximately 0.92 of the peak value. On reverse flushing, this drops to 0.14. With 2 pounds per thousand gallons of encapsulated breaker, the differential pressure immediately starts dropping as soon as the brine flush is started and after 250 pore volumes is 0.3 of the peak value. The same results with 5 ppt gallons loading of encapsulated breaker has a differential pressure of 0.21 of peak value, and with 20 ppt loading has a differential pressure of 0.08 of the peak value. On reverse flushing, the normalized differential pressure of all the tests with the encapsulated breaker present is in the range of 0.014 to 0.025 of the peak values. The pressure differential is directly proportional to the amount and permeability of filter cake, and, thus, this example shows the utility of the encapsulated breaker in reducing filter cake. The fluid in the core itself exhibits minimal differential pressure.

TABLE 4

DIFF. PRESS. ACROSS CORE

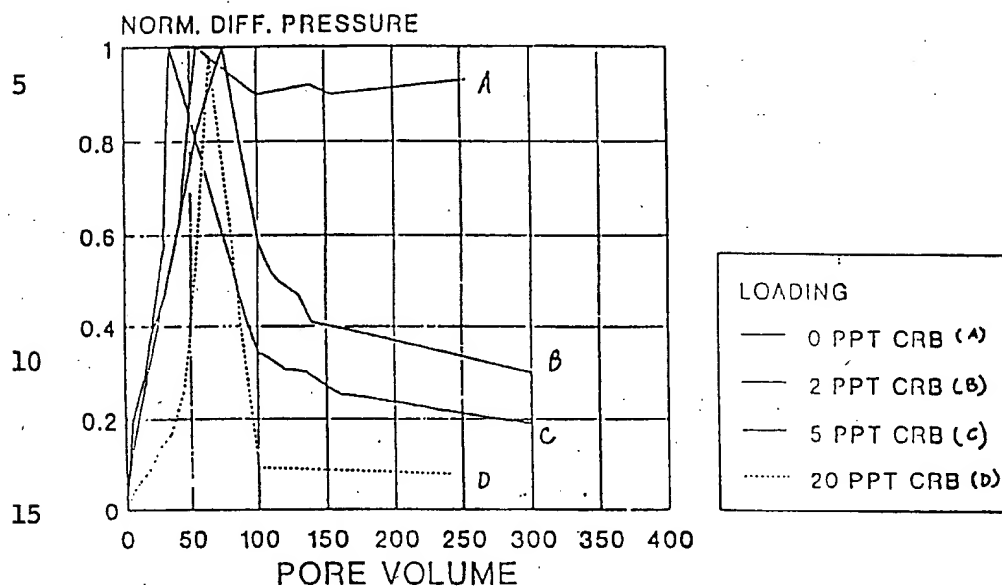
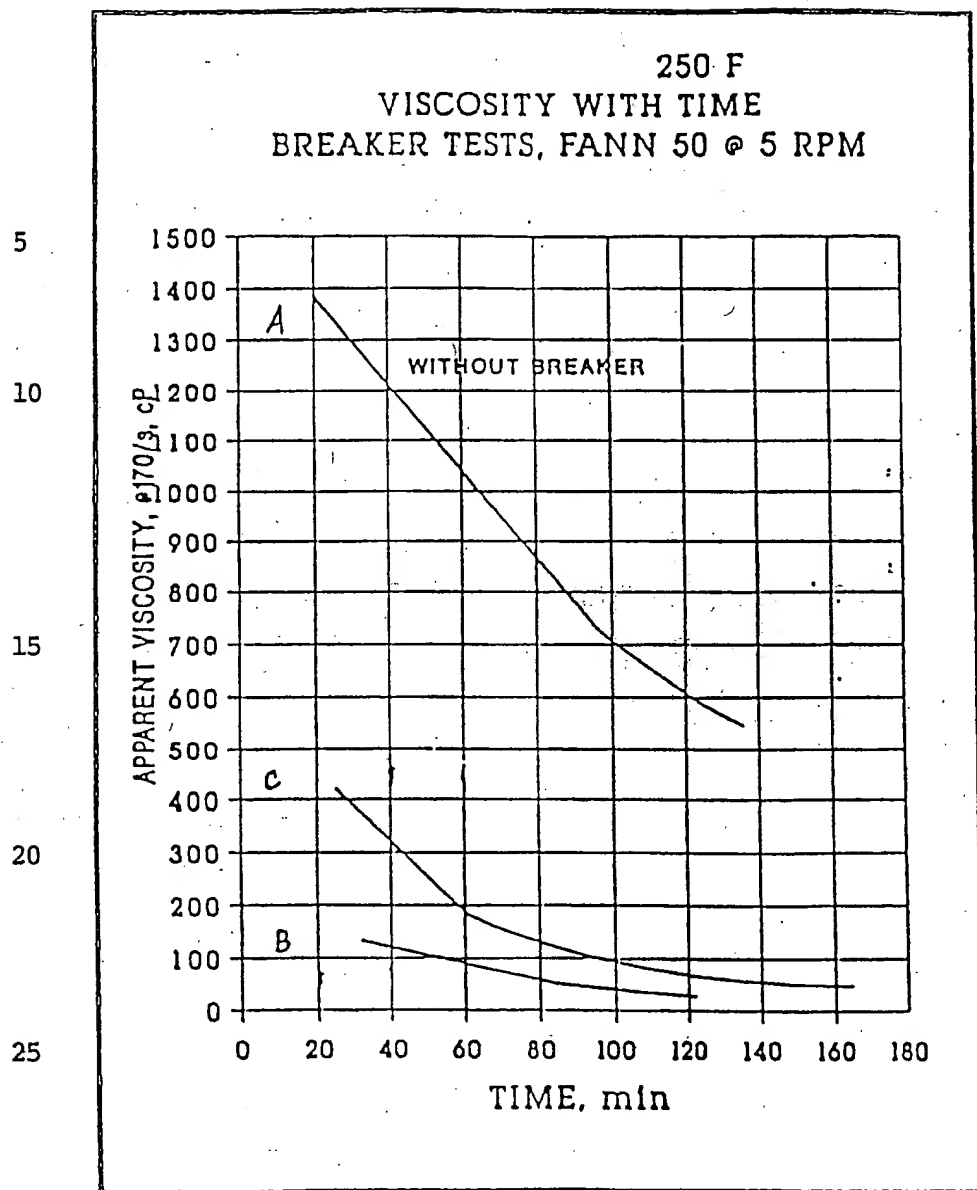


Table 5 shows the effectiveness of the encapsulated breaker in controlling the break of crosslinked fluids at high temperatures.

5 A 60 ppt hydroxypropyl guar base gel is crosslinked with a zirconium crosslinker at pH 9.5 as described in U.S. Patent 4,534,870. 0.5 pounds per thousand gallons of both unencapsulated and encapsulated breakers are added to the crosslinked fluid. The viscosities of these systems are
10 determined by Fann 50 model high-pressure high-temperature rheometer. The results are shown in Table 5. Without the presence of any temperature stabilizers and breakers, the fluid has approximately 600 centipoises at 2 hours at 250°F.
15 (See A.) A loading of 0.5 ppt of unencapsulated breaker, ammonium persulfate, breaks the gel in less than 2 hours. (See B.) The encapsulated breaker, potassium persulfate, controls the viscosity of the system to give a break time of
20 over 3 hours. (See C.)

TABLE 5



While the illustrative embodiments of the invention have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the invention. Accordingly, it is not intended that the scope of claims appended hereto be limited to the examples and descriptions set forth herein but rather that the claims be construed as encompassing all the features of patentable novelty which reside in the present invention, including all features which would be treated as equivalents thereof by those skilled in the art to which the invention pertains.

Claims

1. A method for breaking an aqueous fracturing fluid comprised of introducing an encapsulated breaker into a subterranean formation being
5 treated with the fracturing fluid, said encapsulated breaker comprised of a membrane enclosing the breaker, said membrane being permeable to a fluid in the subterranean formation such that the breaker diffuses through the
10 membrane into the fracturing fluid.
2. The method of claim 1, wherein the breaker is an alkali or alkaline earth metal percarbonate, an alkali or alkaline earth metal perchlorate, an
15 alkali or alkaline earth metal persulfate, or ammonium persulfate.
3. The method of claim 1, wherein the membrane of the encapsulation is a polyamide, a crosslinked ethylene copolymer or a cellulosic material.
4. The method of claim 1, wherein the diameter of
20 the encapsulated breaker is from about 50 to about 420 microns.
5. The method of claim 1, wherein the weight percent of the active breaker contained in the encapsulated breaker is from about 20% to about
25 90%.
6. The method of claim 1, wherein the thickness of the membrane of the encapsulated breaker is from about 5 to about 25 microns.
7. The method of claim 1, wherein the membrane of
30 the encapsulated breaker is comprised of ethylcellulose.
8. The method of claim 1, wherein the membrane of the encapsulated breaker is comprised of nylon.
9. The method of claim 1, wherein the
35 encapsulated breaker is injected into the

subterranean formation with a carrier fluid.

10. The method of claim 9, wherein the encapsulated breaker membrane is permeable to the carrier fluid.

5 11. The method of claim 1, wherein the temperature of the subterranean formation is from about 80°F to 350°F.

12. A method for breaking an aqueous fracturing fluid comprised of introducing into a formation
10 being fractured with the aqueous fluid an encapsulated breaker, said encapsulated breaker comprised of a breaker enclosed within an inert membrane comprised of a polyamide, a crosslinked ethylene copolymer, or a cellulosic material such
15 that the breaker diffuses through the membrane into the fluid.

13. The method of claim 12, wherein the breaker is an alkali or alkaline earth metal percarbonate, an alkali or alkaline earth metal perchlorate, an
20 alkali or alkaline earth metal persulfate, or ammonium persulfate.

14. The method of claim 12 wherein the diameter of the encapsulated breaker is from about 50 to about 420 microns.

25 15. The method of claim 12, wherein the weight percent of the active breaker in the encapsulated breaker is from about 20% to about 90%.

16. The method of claim 12, wherein the thickness of the membrane of the encapsulated breaker is
30 from about 5 to about 25 microns.

17. The method of claim 12, wherein the membrane of the encapsulated breaker is comprised of ethylcellulose or nylon.

35 18. The method of claim 12, wherein the encapsulated breaker is injected into the

subterranean formation with a carrier fluid.

19. The method of claim 18, wherein the encapsulated breaker membrane is permeable to the carrier fluid.

5 20. The method of claim 12, wherein the temperature of the subterranean formation is from about 80°F to 350°F.

10 21. A method for breaking an aqueous fracturing fluid comprised of introducing into a formation being fractured with the aqueous fluid an encapsulated breaker, said encapsulated breaker comprised of a breaker enclosed within a permeable membrane nylon, crosslinked ethylene copolymer or ethylcellulose such that the breaker diffuses
15 through the membrane into the fracturing fluid with the membrane remaining intact.

22. The method of claim 21, wherein the breaker is an alkali or alkaline earth metal percarbonate, an alkali or alkaline earth metal perchlorate, an
20 alkali or alkaline earth metal persulfate, or ammonium persulfate.

23. The method of claim 21, wherein the diameter of the encapsulated breaker is from about 50 to about 420 microns.

25 24. The method of claim 21, wherein the weight percent of the active breaker in the encapsulated breaker is from about 20% to about 90%.

25. The method of claim 21, wherein the thickness of the membrane of the encapsulated breaker is
30 from about 5 to about 25 microns.

26. The method of claim 21, wherein the encapsulated breaker is injected into the subterranean formation with a carrier fluid.

27.. The method of claim 26, wherein the
35 encapsulated breaker membrane is permeable to the

carrier fluid.

28. The method of claim 21, wherein the temperature of the subterranean formation is from about 80°F to 350°F.

5 29. A method for breaking an aqueous fracturing fluid comprised of introducing into a subterranean formation being fractured with the aqueous fluid an encapsulated breaker, said encapsulated breaker consisting of potassium persulfate or ammonium
10 persulfate breaker enclosed within an inert permeable membrane of nylon, crosslinked ethylene copolymer or ethylcellulose, said membrane being permeable to a fluid in the formation such that the breaker diffuses through the membrane into the
15 fracturing fluid with the membrane remaining intact.

30. The method of claim 29, wherein the diameter of the encapsulated breaker is from about 5 to about 25 microns.

20 31. The method of claim 29, wherein the weight percent of the active breaker in the encapsulated breaker is from about 20% to about 90%.

32. The method of claim 29, wherein the thickness of the membrane of the encapsulated breaker is
25 from about 5 to about 25 microns.

33. The method of claim 29, wherein the encapsulated breaker is injected into the subterranean formation with a carrier fluid.

34. The method of claim 33, wherein the
30 encapsulated breaker membrane is permeable to the carrier fluid.

35. The method of claim 29, wherein the temperature of the subterranean formation is from about 80°F to 350°F.

35 36. A method for breaking a fracturing fluid

comprised of introducing into a formation being fractured with the fluid an encapsulated breaker, said encapsulated breaker comprised of a breaker enclosed within a membrane of ethylcellulose, crosslinked ethylene copolymer or nylon such that the breaker diffuses through the membrane into the fracturing fluid with the membrane remaining intact.

37. The method of claim 36, wherein the breaker is an alkali or alkaline earth metal percarbonate, an alkali or alkaline earth metal perchlorate, an alkali or alkaline earth metal persulfate, or ammonium persulfate.

38. The method of claim 36, wherein the diameter of the encapsulated breaker is from about 50 to about 420 microns.

39. The method of claim 36, wherein the weight percent of the active breaker in the encapsulated breaker is from about 20% to about 90%.

40. The method of claim 36, wherein the thickness of the membrane of the encapsulated breaker is from about 5 to about 25 microns.

41. The method of claim 36, wherein the encapsulated breaker is injected into the subterranean formation with a carrier fluid.

42. The method of claim 41, wherein the encapsulated breaker membrane is permeable to the carrier fluid.

43. The method of claim 36, wherein the temperature of the subterranean formation is from about 80°F to 350°F.

44. An encapsulated breaker for breaking an aqueous fracturing fluid used to fracture subterranean formations consisting of a breaker enclosed within a membrane, said membrane being

permeable to the fluid such that when the encapsulated breaker is injected into the formation being treated with the fluid the breaker diffuses through the membrane into the fluid with the membrane staying intact.

45. The encapsulated breaker of claim 44, wherein the breaker is an alkali or alkaline earth metal percarbonate, an alkali or alkaline earth metal perchlorate, an alkali or alkaline earth metal persulfate, or ammonium persulfate.

46. The encapsulated breaker of claim 44, wherein the membrane of the encapsulation is comprised of a polyamide, a crosslinked ethylene copolymer or a cellulosic material.

47. The encapsulated breaker of claim 44, wherein the diameter of the encapsulated breaker is from about 50 to about 420 microns.

48. The encapsulated breaker of claim 44, wherein the weight percent of the active breaker contained in the encapsulated breaker is from about 20% to about 90%.

49. The encapsulated breaker of claim 44, wherein the thickness of the membrane of the encapsulated breaker is from about 5 to about 25 microns.

50. The encapsulated breaker of claim 44, wherein the membrane of the encapsulated breaker is comprised of ethylcellulose.

51. An aqueous crosslinked fracturing composition comprised of water, a crosslinker, a polymer, and an encapsulated breaker, said encapsulated breaker comprised of a breaker enclosed within a membrane of ethylcellulose, crosslinked ethylene copolymer or nylon permeable to the water such that the breaker diffuses through the membrane with the membrane remaining intact.

52. The composition of claim 51, wherein the crosslinker is a borate, a titanate or a zirconate.

5 53. The composition of claim 51, wherein the polymer is guar, hydroxy alkyl guar, carboxy alkyl hydroxy alkyl guar, cellulose, hydroxy alkyl cellulose, carboxy alkyl hydroxy alkyl cellulose or xanthan.

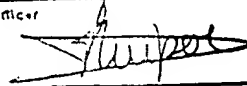
10 54. The composition of claim 51, wherein the breaker is an alkali or alkaline earth metal percarbonate, an alkali or alkaline earth metal perchlorate, an alkali or alkaline earth metal persulfate, or ammonium persulfate.

15 55. The composition of claim 51, wherein the thickness of the membrane of the encapsulated breaker is from about 5 to about 25 microns.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/08818

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁴		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC ⁵ : E 21 B 43/27		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	E 21 B, C 09 K	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
A	US, A, 4 741 401 (WALLES et al.) 03 May 1988 (03.05.88), see abstract; column 4, line 67 - column 5, lines 4,46-60 (cited in the application).	1-3,7, 9,10, 12,13, 17-19, 21,22, 27,29, 33,34, 36,37, 41,42, 44-46, 50,51, 53,54
X	US, A, 4 770 796 (JACOBS) 13 September 1988 (13.09.88), see claims 1,5,10,11,15; column 5, lines 14-18 (cited in the application).	1,3,7, 10,12, 17-19, 21,27, 29,33, 36,41, 42,44, 46,50- 52
<p>¹⁰ Special categories of cited documents: ¹⁴</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"Z" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
31 March 1992	15 APR 1992	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	Mm N. KUIPER 	

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/US91/08818 SAE 54903

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
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This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
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La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
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national visée ci-dessus. Les renseigne-
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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
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